

Soft X-ray absorption spectroscopy of *single* nanocrystals

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INTRODUCTION

A common limitation in nanostructure research is often the requirement to perform experiments on ensembles of nanoparticles, therefore averaging over inherent distributions with respect to particle size and shape, chemical composition, crystallinity and defect structure. This limitation can be overcome by studying the properties of a single nanostructure individually, which will allow to truly correlate scaling laws of material properties with changes in size. Here, we demonstrate the applicability of spatially resolved Photoemission Electron Microscopy (PEEM) to measure soft x-ray absorption spectra at the Fe $L_{3,2}$ edges of *single* colloidal iron oxide nanocrystals with an average diameter of 10 nm ($\sim 20,000$ iron atoms). The experiment was carried out with the PEEM2 instrument of the ALS [1]. Details of the experiment can be found in [2,3].

EXPERIMENT

Surfactant-capped nanocrystals of $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) were prepared by a slightly modified version of a recently published procedure using hexadecylamine as surfactant [4]. A fraction was isolated by repeated size-selective precipitation using methanol as precipitating agent and the average particle size was determined by TEM to be 10 nm with a standard deviation of 3 nm. Very dilute toluene solutions of this sample were spin-coated onto silicon wafers that were freshly cleaned by etching with HF and washing with deionized H_2O . The particle coverage of the silicon substrate was determined by high-resolution Scanning Electron Microscopy (SEM) at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory. From the relative positions of the particles in the SEM images (Fig 1A), a mean first nearest neighbor distance of 485 nm was derived. This is sufficiently larger than the spatial resolution of the PEEM microscope in this study. In contrast to our first study [2,5] using graphite as substrate, we were never able to resolve these spots into smaller aggregates indicating that they, indeed, represent individual nanocrystals. Also, linescans through individual spots show FWHM in the range of 8 – 15 nm in good agreement with the particle size distribution of the sample as determined by TEM.

The PEEM experiments were performed at the bending magnet beamline 7.3.1.1 of the ALS. The best lateral spatial resolution achieved by PEEM to date is about 20 nm, but it depends strongly, in addition to the settings of the instruments, on the topography and conductivity of the sample. In the studies presented here, the spatial resolution was about 150 nm. Fig. 1B shows a chemical contrast image which was obtained by subtracting an image taken at a pre-edge photon energy (700 eV) from the one taken at the iron L_3 edge (707 eV). Hence, the bright spots indicate the presence of iron oxide nanocrystals. The varying brightness of the spots is most likely related to the rather broad size distribution of the iron oxide nanocrystals in the sample with an average diameter and a standard deviation of 10 nm and 3 nm, respectively. In Fig. 1C, the local x-ray absorption spectra of a location appearing bright in Fig 1B (area I) is compared to the one of a dark area (area II). As expected, the spectrum of the bright spot (area I) shows the signature of the Fe L_3 absorption edge

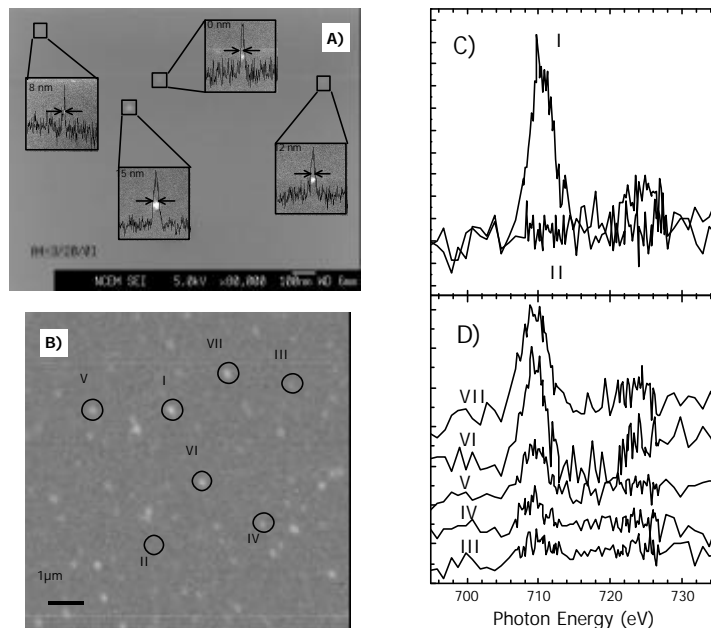


Figure 1: a) High-magnification SEM image of γ -Fe₂O₃ nanocrystals deposited onto Silicon wafer. B) PEEM chemical contrast image. C) Spatially resolved X-ray absorption spectrum recorded in a bright area (I) and a dark area (II). D) Local spectra for different bright spots in b).

at 707 eV, whereas the dark background (area II) shows no detectable structure of the absorption intensity in this energy range. Due to the moderate energy resolution, the multiplet structure of the typical x-ray absorption spectra of Fe³⁺-ions at the L₃-edge is not resolved. In Fig. 1D, the x-ray absorption spectra of several positions with varying intensities in Fig. 1B (areas III - VII) are compared. Clearly, even in cases with very small intensity in the contrast image in Fig. 1B the Fe L₃ x-ray absorption edge is still discernible from the background whereas the weaker L₂ edge is only barely recognizable. We emphasize that these spectra indeed reflect the x-ray absorption spectra of individual particles with diameters of (10 ± 3) nm with a small chance that some spectra are due to the presence of dimers or trimers of particles ($< 13\%$) [3]. To the best of our knowledge, this represents the first time that soft x-ray absorption spectra of individual nanocrystals at this length scale are reported [6].

This work was supported by the Director, Office of Basic Energy, Division of Chemical Sciences and the Division of Materials Sciences of the U.S. Department of Energy, the Air Force Office of Scientific Research, and the Deutsche Forschungsgemeinschaft.

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- [6] Recently, x-ray photoemission spectra of InAs nanocrystals were reported by Heun *et al.*, Phys. Rev. B **2001**, 63, 125335. They presented averages spectra over all InAs nanocrystals imaged. Also, the InAs nanocrystals with an average diameter and height of 55 nm and 22 nm, respectively, contain significantly more atoms (factor of 40) than the 10 nm γ -Fe₂O₃ nanoparticles investigated here.